Using noble gases to analyze the efficiency of artificial aeration in Lake Hallwil, Switzerland

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[1] Eutrophic Lake Hallwil (Switzerland) is equipped with an artificial aeration system to prevent anoxic conditions developing in the deep water during stratification in summer. The aeration system consists of diffusers releasing oxygen-rich gas containing noble gases into the deep water at the bottom of the lake. The deep water is strongly supersaturated with He, Ne, and Ar, while Kr and Xe are present at concentrations corresponding to their respective atmospheric equilibria. The observed noble gas excesses are related to the operation of the aeration system and to the composition of the injected aeration gas. We show how noble gas data were used successfully to estimate the fraction of the injected aeration gas that effectively remains dissolved in the water body. In particular, as the physical properties of Ar (e.g., atomic mass, solubility, diffusion coefficient) are similar to those of oxygen, the measured noble gas concentrations allow the efficiency of the aeration system to be quantified.

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1. Introduction

[2] Lake Hallwil is a medium-sized lake located in central Switzerland (47° 17′N, 8° 13′E, 449 m above sea level, volume 285 × 10^6 m^3, surface area 9.95 × 10^6 m^2, maximum water depth 46.5 m; see Figure 1). The lake became eutrophic around the beginning of the 20th century as a result of the increasing input of phosphorus from municipal wastewater and agriculture [*Märki and Schmid*, 1983]. The high nutrient input to the lake led to extensive algal production and subsequent mineralization, which caused oxygen (O_2) depletion in the hypolimnion.

[3] As external restoration measures to reduce the nutrient input to the lake were not sufficient to prevent anoxic conditions developing, an aeration system was installed in 1985 [*Stöckli and Schmid*, 1987; *Schaffner*, 1987; *Wehrli and Wüest*, 1996] to guarantee minimum O_2 concentrations in the water column. This system consists of six diffusers, each with a diameter of 6.5 m, that are installed in a circular configuration 300 m wide at the deepest part of the lake (Figure 1). The aeration gas is compressed on the shore and directed to the diffusers through pipes at the lake bottom. The diffuser system aims to increase O_2 concentrations in Lake Hallwil in two different ways [*Scheidegger et al.*, 1994].

[4] In winter, compressed air is injected into the lake as large bubbles to support the vertical water circulation. The air injection forces a plume of bubbles to rise above the diffusers, resulting in the upwelling of deep water with low O_2 concentrations due to the buoyancy of the injected air. The transport of O_2-depleted deep water to the surface enhances oxygenation by "natural" gas partitioning with the atmosphere. Note that large-scale seasonal mixing in Lake Hallwil, and therefore natural gas exchange, is limited because the lake is located in a north-south oriented valley, which protects the lake against the predominant westerly winds.

[5] During summer, the system injects smaller oxygen-enriched gas bubbles that are presumed to dissolve almost completely in the deep-water body below the thermocline (hypolimnion). The gas flow rate of the system is regulated such that the rising bubble plume does not affect the stratification of the water column, but the O_2 input is sufficient to prevent anoxic conditions occurring in the deep water. Due to the relatively high productivity of the lake and the subsequent decomposition of organic matter, the injected O_2 is consumed very rapidly in the hypolimnion and no significant O_2 accumulation within the plume is directly detectable. Between 2003 and 2009 the aeration system was equipped and operated with an on-site O_2 enrichment that produces aeration gas containing ~80% O_2 by removing most of the nitrogen from the compressed air.

[6] The internal (diffusor system) and external (reduction of nutrient input) measures resulted in a significant improvement in lake water quality since the start of the remediation program.

[7] Despite the reduced nutrient concentrations, the oxygen consumption again increased considerably after 1999 because of a massive bloom of *Planktothrix rubescens*

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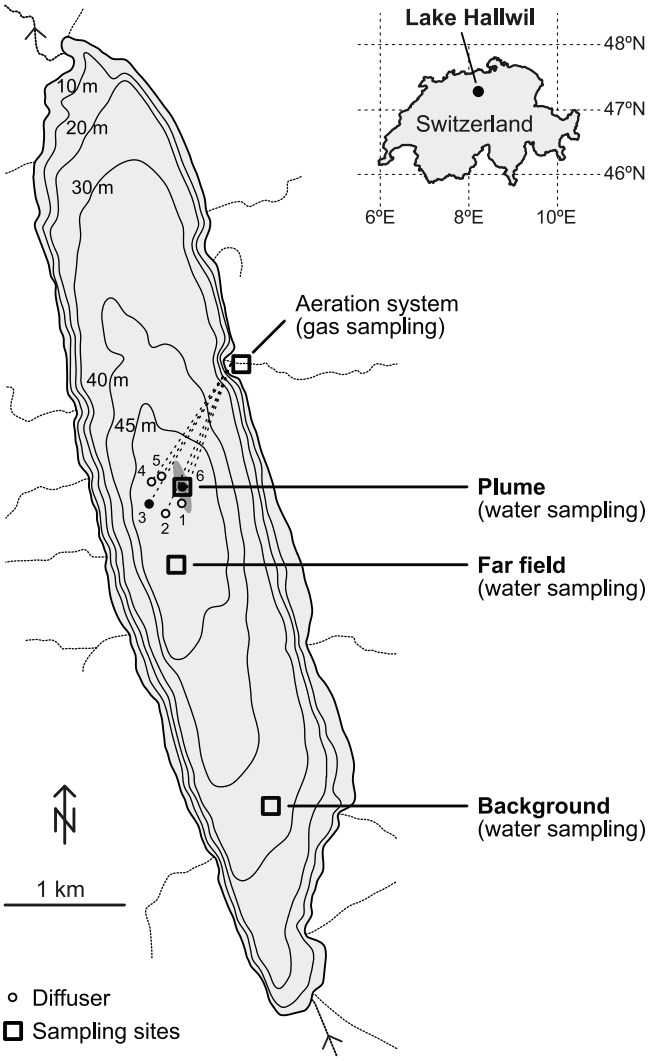

Figure 1. Map of Lake Hallwil, showing the positions of the diffusers (1–6) and of the sampling sites. A darker ellipse around diffuser 6 indicates the zone that is affected by the aeration gas input during the 2 day "high flow" phase. The inset shows the location of Lake Hallwil in Switzerland.

[*Stöckli*, 2005]. This cyanobacterium was common in Lake Hallwil in the first half of the 19th century but had disappeared as the nutrient concentrations became very high. In this context, the reappearance of *P. rubescens* is indicative of better water quality. However, the nutrient concentrations in the lake need to be reduced further if the use of the aeration system is to be rendered unnecessary.

[8] Currently, the circulation support in winter and oxygenation in summer are still needed to fulfill the legal water quality objective of 4 mg/L O_2 throughout the entire water column [*Der Schweizerische Bundesrat*, 1998].

[9] The progress of the restoration measures in Lake Hallwil is monitored by the Department of Civil Engineering, Transportation and Environment of the Canton of Argovia (see http://www.ag.ch/umwelt), based on regular measurements of various physical, chemical and biological variables in the lake. The routine monitoring was complemented with noble gas measurements in 2005 to quantify the efficiency of the aeration system.

[10] We measured helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe) both in the aeration gas and dissolved in the water of the lake, to study the effect of the injection of the aeration gas on the noble gas concentrations in Lake Hallwil during summer stratification. We show that the concentrations of dissolved noble gases may be used to estimate the total mass of gas that is transferred from the injected bubbles to the aqueous phase during aeration (i.e., noble gas enrichment can be interpreted as a proxy for the transfer of O_2 to the lake water). A noble gas mass balance suggests that the injected aeration gas is efficiently dissolved in the lake during summer stratification and that gas loss to the atmosphere is likely to be negligible.

[11] The concentrations of dissolved atmospheric noble gases in lakes commonly correspond to the equilibrium concentrations calculated for the atmospheric pressure at the surface of the lake, and the temperature and salinity that prevail during gas exchange between the lake and the atmosphere [*Aeschbach-Hertig et al.*, 1999; *Kipfer et al.*, 2002]. As noble gases are chemically inert under common environmental conditions, the noble gas concentrations can be altered only by physical processes or by the additional input of noble gases from nonatmospheric sources, which are therefore responsible for any deviations from atmospheric equilibrium [*Kipfer et al.*, 2002]. Gas bubbles that are injected into a lake will affect the concentrations of dissolved gases in the water column as the bubbles strip gases from the surrounding water and simultaneously dissolve during their ascent [*Wüest et al.*, 1992; *Clark et al.*, 2003; *McGinnis et al.*, 2006;*Holzner et al.*, 2008]. The effect of these secondary gas-exchange processes on the concentrations of dissolved gases varies according to the solubility and diffusivity of each of the gases involved, and also depends on the initial gas concentrations in the bubbles. We therefore expect the signals of dissolved noble gases in Lake Hallwil to be characteristic of the prevailing aeration gas flow rate and the composition of the aeration gas. Especially during summer stratification, when gas exchange with the atmosphere is limited, affecting the concentrations in the mixed surface water body above the thermocline (i.e., in the epilimnion), dissolved noble gases in the hypolimnion are expected to form an "archive" of the history of the preceding aeration operation. In winter, the noble gas concentrations in the lake are expected to be reset to the atmospheric equilibrium concentrations that result from vertical mixing and gas exchange with the atmosphere. Since 1986 Lake Hallwil has had no winter ice cover [*Hendricks Franssen and Scherrer*, 2008]. In addition, the winter circulation mode produces an advective water flow that would hamper the formation of ice. Anomalies in the concentrations of dissolved noble gases resulting from a reduced gas exchange with the atmosphere in winter [e.g., *Malone et al.*, 2010] are therefore not expected.

2. Methods

2.1. Sampling

[12] Samples for the analysis of noble gas concentrations were collected during one week in July 2005. Our sampling was coordinated with a series of physical measurements in Lake Hallwil (transects of CTD profiles, vertical current

Table 1. Operation of the Aeration System During the Sampling Campaign

Time Interval	J_{tot}[a] [Nm^3/hr]	J_{diff}[b] [Nm^3/hr]	Remarks
05 April–11 July 2005 10:20	72	12	**normal flow** rate to all 6 diffusers, sampling on 08 July
11–12 July 2005 10:30	62	31	high flow rate to diffusers 3 and 6 only
12–13 July 2005 12:30	0	0	**aeration off** for 26 h, sampling on 13 July
13–15 July 2005 14:35	56	28	**high flow rate** to diffusers 3 and 6 only, sampling on 15 July
After 15 July 2005	72	12	normal flow rate to all 6 diffusers

[a] J_{tot}, gas flow rate to all diffusers; 1 Nm^3 (i.e., gas at 0°C and 1 atm) ≙ 10^6 cm^{3}STP.
[b] J_{diff}, gas flow rate to each active diffuser.

velocity profiles using an acoustic Doppler velocimeter, and thermistor moorings) to collect data to refine a numerical bubble plume model [*McGinnis et al.*, 2004; T. Edmonds and V. Singleton, Virginia Polytechnic Institute and State University, unpublished report, 2005]. During the field campaign, the gas flow of the aeration system was either set to rates higher than those used during normal oxygenation operation in summer or was switched off completely (see Table 1). We collected three depth profiles of water samples for noble gas analysis and two aeration gas samples on 08 July 2005, prior to the physical measurements when the system was still being operated at the normal aeration gas flow rate used during the summer season (referred to as "normal flow" in the following). The water samples were taken at three sites that lay approximately along the longitudinal axis of the lake (Figure 1). The "plume" site was located above diffuser number 6 of the aeration system. The "far field" site was located ∼600 m and the "background" site ∼2.7 km south of the aeration system. Water sampling at all three sites was repeated on 13 July 2005, after the aeration system had been inactive for ∼1 day ("aeration off"), and on 15 July 2005, after ∼2 days of increased aeration gas flow rate ("high flow"). During this "high flow" phase, the aeration gas was directed only to diffusers number 3 and 6 to increase the gas flow per diffuser by a factor of ∼3 while keeping the total gas flux into the lake virtually constant. We also sampled the aeration gas on 13 July 2005 and on 15 July 2005.

[13] Water samples for noble gas analysis were taken using Niskin bottles, avoiding any air contamination during sampling. On the ship, the water samples were immediately transferred to copper tubes that were sealed gas-tight using pinch-off clamps [*Beyerle et al.*, 2000]. Gas samples were withdrawn from the gas supply of the aeration system and likewise stored in sealed copper tubes.

[14] CTD profiles measured using a Seabird SBE19 probe at the positions of the water sampling stations were provided by the Department of Civil Engineering, Transportation and Environment of the Canton of Argovia for 08 July 2005 and by the team of the physical measurement campaign for 13 July 2005 and 15 July 2005 [T. Edmonds and V. Singleton, unpublished report, 2005].

2.2. Noble Gas Analysis

[15] The concentrations of He, Ne, Ar, Kr, and Xe both in the aeration gas and dissolved in the water samples were determined by static mass-spectrometry [*Beyerle et al.*, 2000]. In total, 48 water samples and 4 gas samples were analyzed. Typical overall errors in the noble gas concentration measurements (1σ errors) are ±1–2%. The measurements for the aeration gas sampled on 15 July 2005 were not used in this study because of the occurrence of a technical problem in the aeration system during gas sampling that prevented reliable noble gas determination.

[16] To calculate the atmospheric equilibrium concentrations of noble gases in water, we used the parameterizations recommended by *Kipfer et al.* [2002]. The dissolved noble gas concentrations presented in this study are normalized to the equilibrium concentrations corresponding to the measured temperature and salinity (Table 2), and to a mean atmospheric pressure of 0.95 atm (corresponding to 449 m a.s.l.).

3. Results and Discussion

3.1. Differences in the Noble Gas Concentration Profiles Along the Lake Axis

[17] The noble gas profiles sampled during "normal flow" operation at three sites in Lake Hallwil show a distinct variation in the He, Ne, and Ar concentrations related to the distance from the aeration system (Figure 2a, Table 3). Water samples from the hypolimnion are supersaturated in He, Ne, and Ar at all three stations; i.e., the observed concentrations exceed the local equilibrium concentrations. The magnitude of the noble gas enrichment decreases with increasing distance from the bubble plume. No enrichment of He, Ne, and Ar occurs above the thermocline ($z < 10$–15 m). In contrast, the Kr and Xe concentrations are close to equilibrium with the atmosphere at all depths and the concentration profiles from the three sites agree within analytical errors. The slightly higher saturations observed for Kr and Xe in the uppermost samples in the epilimnion and in the thermocline indicate that the water mass at these depths had not yet completely reached atmospheric equilibrium with respect to the local temperature conditions. In fact, gas loss from the water body to the atmosphere in response to the heating of the upper part of the water column during summer is still ongoing, as indicated by the concentration gradient in the uppermost ∼10 m (see Figure 2a and Table 3).

[18] The observed supersaturations of He, Ne and Ar in the hypolimnion correspond to the relative elemental composition of the aeration gas (Table 4). Noble gases in the injected gas bubbles are strongly fractionated with respect to atmospheric air. He, Ne, and Ar in the aeration gas are enriched by a factor of 3–4, whereas Kr and Xe are virtually absent (i.e., their volume fractions are nearly zero). Hence, the enrichment of He, Ne, and Ar relative to the composition of atmospheric air is in the same range as the enrichment of O_2. The on site O_2 enrichment unit of the aeration system that is active during oxygenation in summer, together with the removal of nitrogen, seem also to contribute to the prominent mass fractionation of the injected noble gases. Apparently, the heavy noble gases Kr and Xe are removed from the aeration gas, whereas the lighter noble gases He, Ne, and Ar are enriched together with the O_2.

Table 2. Temperatures, T, and Salinities, S, Measured in the Water Column of Lake Hallwil During the Sampling Campaign

08 July 2005			13 July 2005			15 July 2005		
normal aeration gas flow rate			aeration off			high aeration gas flow rate		
z [m]	T [°C]	S [g/kg]	z [m]	T [°C]	S [g/kg]	z [m]	T [°C]	S [g/kg]
				Plume Site				
1	21.13	0.229	1	20.88	0.228	1	22.07	0.229
10	9.88	0.258	10	9.94	0.259	5	21.29	0.228
15	5.27	0.265	15	5.53	0.265	10	9.56	0.259
20	4.84	0.267	20	4.99	0.264	15	5.63	0.263
30	4.66	0.268	30	4.69	0.263	25	4.77	0.263
40	4.57	0.269	40	4.51	0.265	40	4.58	0.264
				Far Field Site				
1	21.22	0.230	1	20.96	0.228	1	22.21	0.228
10	10.43	0.257	10	9.33	0.261	7.5	14.73	0.240
20	5.08	0.265	20	5.17	0.264	15	5.53	0.263
25	4.79	0.265	25	4.77	0.263	20	4.81	0.263
35	4.59	0.265	35	4.50	0.263	30	4.52	0.263
40	4.57	0.266	40	4.48	0.264	40	4.46	0.267
				Background Site				
1	21.18	0.229	1	21.12	0.228	1	22.83	0.229
20	5.33	0.262	20	4.87	0.262	17.5	5.26	0.264
25	4.82	0.263	25	4.52	0.261	22.5	4.71	0.263
32	4.58	0.264	32	4.46	0.263	32	4.49	0.263

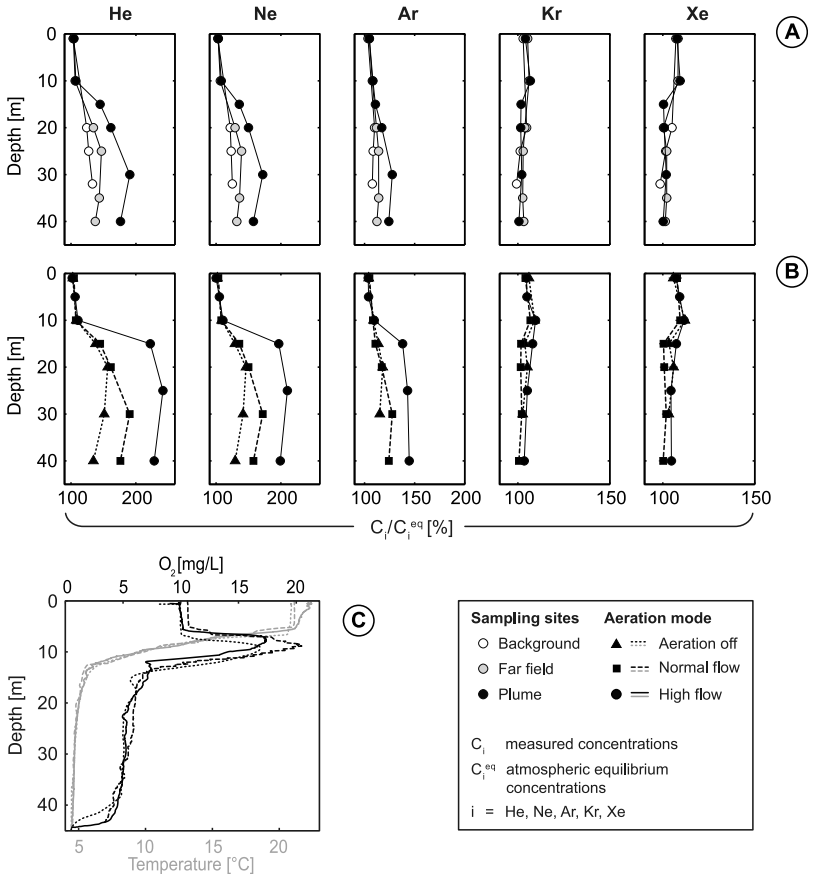

Figure 2. (a) Comparison of the observed noble gas concentration profiles at the three sites while the aeration system was operated in "normal flow" mode. (b) Comparison of the dissolved noble gas concentration profiles at the plume site for three different aeration gas flow rates (i.e., "normal flow", "aeration off", and "high flow"). (c) Comparison of the profiles of temperature and dissolved O_2 concentration at the plume site for the three aeration gas flow rates (the high O_2 concentrations in the thermocline are the result of biogenic production).

Table 3. Concentrations of He, Ne, Ar, Kr, and Xe Measured in the Water Column of Lake Hallwil at Depths z[a]

08 July 2005						13 July 2005						15 July 2005					
normal aeration gas flow rate						aeration off						high aeration gas flow rate					
	Concentrations [cm^3_{STP}/g]						Concentrations [cm^3_{STP}/g]						Concentrations [cm^3_{STP}/g]				
z [m]	He [10^{-8}]	Ne [10^{-7}]	Ar [10^{-4}]	Kr [10^{-7}]	Xe [10^{-8}]	z [m]	He [10^{-8}]	Ne [10^{-7}]	Ar [10^{-4}]	Kr [10^{-7}]	Xe [10^{-8}]	z [m]	He [10^{-8}]	Ne [10^{-7}]	Ar [10^{-4}]	Kr [10^{-7}]	Xe [10^{-8}]
Plume Site																	
1	4.41	1.80	3.02	0.67	0.94	1	4.34	1.77	3.02	0.68	0.92	1	4.28	1.72	2.94	0.65	0.91
10	4.72	2.06	3.97	0.92	1.37	10	4.76	2.07	3.98	0.94	1.40	5	4.49	1.82	2.99	0.67	0.94
15	6.51	2.72	4.54	1.01	1.48	15	6.19	2.58	4.63	1.02	1.51	10	4.88	2.12	4.04	0.95	1.41
20	7.27	3.02	4.85	1.02	1.51	20	7.05	2.94	4.87	1.05	1.58	15	9.97	3.92	5.60	1.06	1.57
30	8.59	3.47	5.31	1.03	1.54	30	6.82	2.85	4.78	1.03	1.56	25	10.89	4.23	5.93	1.06	1.57
40	7.95	3.18	5.18	1.02	1.52	40	6.08	2.61	[b]	[b]	[b]	40	10.30	4.02	6.03	1.05	1.59
Far Field Site																	
1	4.37	1.79	3.02	0.67	0.94	1	4.28	1.76	3.00	0.67	0.94	1	4.30	1.75	2.98	0.66	0.93
10	4.66	2.03	3.90	0.90	1.33	10	4.68	2.05	3.93	0.93	1.36	7.5	4.50	1.90	3.47	0.79	1.13
20	6.05	2.59	4.60	1.03	1.49	20	5.93	2.67	4.63	1.04	1.51	15	5.11	2.25	4.30	1.00	1.48
25	6.62	2.80	4.72	1.03	1.54	25	5.95	2.55	4.57	1.03	1.55	20	6.15	2.64	4.66	1.03	1.53
35	6.48	2.75	4.75	1.04	1.55	35	6.20	2.60	4.58	1.01	1.51	30	6.64	2.80	4.79	1.05	1.54
40	6.20	2.66	4.68	1.04	1.54	40	5.98	2.59	4.60	1.04	1.53	40	5.96	2.55	4.63	1.04	1.55
Background Site																	
1	4.37	1.78	2.98	0.66	0.93	1	4.30	1.74	2.94	0.64	0.90	1	4.12	1.68	2.84	0.63	0.89
20	5.58	2.44	4.50	1.04	1.55	20	5.40	2.36	4.46	1.04	1.52	17.5	5.26	2.32	4.43	1.04	1.51
25	5.74	2.48	4.50	1.02	1.53	25	5.76	2.47	4.56	1.04	1.53	22.5	5.74	2.47	4.54	1.04	1.56
32	6.00	2.52	4.49	1.00	1.49	32	6.17	2.63	4.66	1.04	1.55	32	5.55	2.39	4.37	1.00	1.49

[a]The overall measurement errors (1σ errors) are ±0.7% for He, ±1.7% for Ne, ±0.6% for Ar, ±1.3% for Kr, and ±2.2% for Xe. STP = standard temperature (0°) and pressure (1 atm).
[b]Lost as a result of experimental problems.

[19] To summarize, the injection of the aeration gas into the lake and the dissolution of the gas bubbles rising in the water column seem to cause an accumulation of He, Ne and Ar in the hypolimnion. This effect is greatest for profiles sampled directly above one of the aeration system diffusers; i.e., within the bubble plume. As noble gases are chemically conservative, the "aeration signal" persists in the hypolimnion of Lake Hallwil during summer stratification.

[20] The analysis of the elemental ratios of He/Ne and Ne/Ar observed in the aeration gas and in the dissolved gas excess at the plume site emphasizes the likelihood of a causal relationship between the injection of the aeration gas and the supersaturation of the lake with noble gases. The measured noble gas ratios are presented in Table 5. At normal aeration gas flow rates, the elemental ratios of He/Ne and Ne/Ar in the gas excess in the hypolimnion agree with the ratios in the injected aeration gas. This suggests that the injected noble gases either dissolve completely below the thermocline or escape from the lake in equal proportions. However, if gas loss were to occur, this effect would not influence all the noble gases equally because of the considerable differences in their solubilities. Gas loss would mainly affect the less soluble light noble gases He and Ne, and would therefore lead to the preferential accumulation of Ar in the lake water. The accumulation of Ar would result in a Ne/Ar ratio for the noble gas excess in the water that is lower than the ratio in the injected gas. As the noble gas ratios in the aeration gas and in the noble gas excess of the hypolimnion closely match, the occurrence of considerable gas loss appears to be very unlikely. During oxygenation in summer, the aeration system is continuously monitored and adjusted to assure that the injected aeration gas bubbles completely dissolve in the hypolimnion. During the oxygenation period from 05 April 2005 to 08 July 2005 that preceded our sampling, no gas bubbles escaping at the lake surface (which would have caused considerable gas loss) were observed. To sum up, our

Table 4. Elemental Composition of the Aeration Gas[a]

Gas i	v_i^{gas} [b]	v_i^{gas}/v_i^{air} [c]
He	1.66×10^{-5}	3.17
Ne	5.73×10^{-5}	3.15
Ar	3.80×10^{-2}	4.07
Kr	1.14×10^{-8}	0.01
Xe	2.96×10^{-9}	0.03
O_2	7.72×10^{-1}	3.69

[a]O_2 data were provided by the Department of Civil Engineering, Transportation and Environment of the Canton of ArgoviaListed values of v_i^{gas} are mean values for the samples collected on 08 July 2005 and 13 July 2005. The noble gas fractions of the three analyzed aeration gas samples vary by less than 3%. Noble gases and O_2 comprise ~81% of the aeration gas volume; the composition of the remaining ~19% was not determined, under the assumption it was mostly nitrogen.
[b]v_i^{gas}, volume fraction in the aeration gas.
[c]v_i^{air}, volume fraction in air.

Table 5. Comparison of He/Ne and Ne/Ar Elemental Ratios in the Aeration Gas and in the Dissolved Gas Excess in the Water Column

Gas Reservoir	He/Ne × 10	Ne/Ar × 1000
Aeration gas	2.90 ± 0.05	1.51 ± 0.05
Excess ("normal flow")[a]	2.83 ± 0.09	1.36 ± 0.20
Excess ("high flow")[a]	2.87 ± 0.03	1.19 ± 0.10

[a]Mean ratio of the noble gas excess concentrations at the plume site $C_i^{ex} = C_i - C_i^{eq}$, where i = He, Ne, Ar. C_i are the observed noble gas concentrations and C_i^{eq} are the atmospheric equilibrium concentrations. Only samples from the hypolimnion (depth >15 m) were analyzed, as the noble gas supersaturations occur below 15 m.

findings imply a rather complete dissolution of the injected aeration gas bubbles in the hypolimnion at the normal aeration gas flow rate, and thus an efficient and complete O_2 transfer into the deep water.

3.2. Noble Gas Profiles Observed at Different Aeration Gas Flow Rates

[21] The noble gas concentration profiles sampled at the plume site (i.e., above diffuser 6) under "normal flow", "aeration off" and "high flow" conditions show a strong response of dissolved He, Ne, and Ar concentrations to the variation in the aeration gas flow rate (Figure 2b, Table 3). Compared to the "normal flow" situation, the concentrations of He, Ne, and Ar in the hypolimnion increase considerably at high aeration gas flow rates and decrease substantially if the aeration system is turned off. Because Kr and Xe are missing in the injected gas (Table 4), the concentrations of Kr and Xe in the lake are not affected by the artificial aeration process. The relative increase of the concentrations of the light noble gases He and Ne that occurs with increasing aeration gas flow rate is much more pronounced than for Ar. As He and Ne are less soluble than Ar in water, the accumulation of noble gases in response to aeration contributes a larger share to the total mass of the light noble gases stored in the lake. The short periods of altered aeration gas flow rates did not lead to significant changes in the noble gas concentrations at the far field and background sites (Table 3).

[22] During the period of "high flow", the elemental ratios of Ne/Ar in the noble gas excess measured in the hypolimnion at the plume site were significantly lower then the Ne/Ar ratio in the injected aeration gas (Table 5). By contrast, the respective He/Ne ratios agree to within experimental error. At high aeration gas flow rates, the noble gas excess at the plume site therefore contains a lower Ne fraction with respect to the dissolved Ar fraction, which causes the low Ne/Ar ratio. The shift in the elemental ratios indicates incomplete dissolution of the injected aeration gas bubbles and loss of aeration gas at the lake surface, resulting in an enrichment of more soluble Ar with respect of the less soluble He and Ne. A partial loss of aeration gas to the atmosphere would therefore imply a preferential loss of the sparingly soluble gases that tend to remain in the gas bubbles [*Graser*, 2006; *Holzner et al.*, 2008]. Hence, the observed differences in the noble gas ratios suggest that, at high-aeration gas flow rates, part of the injected gas bubbles did not dissolve completely and escaped to the atmosphere. This is in agreement with the visual observation of small gas bubbles reaching the lake surface at the plume site during "high flow" conditions.

[23] In contrast to the noble gas concentration profiles at the plume site, the profiles of dissolved O_2 remained virtually unchanged despite the strong variation in the aeration gas flow rate (but not in the total mass of injected O_2) during the field campaign (Figure 2c). This implies that even the additional local O_2 input due to the increased aeration gas flow rate is immediately balanced by the high O_2 consumption rate and by the horizontal water transport in Lake Hallwil [*McGinnis et al.*, 2004].

3.3. Mass Balance Calculations

[24] We performed simple noble gas mass balance calculations to obtain a semiquantitative estimate of the accumulation of dissolved gases in Lake Hallwil during the aeration phase. As shown, the hypolimnion is supersaturated with dissolved He, Ne, and Ar owing to the dissolution of injected aeration gas bubbles (Figure 2). The observed noble gas excesses can therefore be interpreted as a measure of the fraction of aeration gas that is stored in the water mass below the thermocline. To determine the noble gas excess concentrations $C_i^{ex} = C_i - C_i^{eq}$ (i = He, Ne, Ar), the measured noble gas concentrations C_i were reduced by the corresponding atmospheric equilibrium concentrations C_i^{eq}. Data from the water sample profiles collected during "normal flow", "aeration off", and "high flow" operation were used to derive a coarse estimate of the excess concentration distribution in the lake on each day. We interpolated noble gas excess concentrations from the three sites linearly in two dimensions on a vertical plane that extends from the plume site to the background site and farther to the lake shore. It should be noted that, as a consequence of the use of linear interpolation, our estimate represents the upper limit of the possible gas accumulation. It was assumed that the noble gas concentrations at the lake surface and at the lake shore are in equilibrium with the atmosphere, and the noble gas excesses produced by the aeration system there are therefore zero. We further assumed that the noble gas excess distributions are symmetric around the plume; i.e., that the excess concentrations are equal on ellipses centered at the bubble plume that have the same width-to-length ratio as Lake Hallwil. The interpolated concentration distributions were integrated over the entire lake volume to estimate the total mass of excess noble gases stored in the lake at the time of sampling. The mass balance calculations were carried out only for He, Ne, and Ar, as Kr and Xe concentrations are not affected by the aeration (i.e., $C_j^{ex} \sim 0$ with j = Kr, Xe).

[25] The resulting estimate of the mass of excess noble gases in Lake Hallwil determined for "normal flow" conditions on 08 July 2005 was compared to the total noble gas mass flux into the lake during the preceding oxygenation period. On 05 April 2005, the aeration system was switched from "circulation support" mode to "oxygenation" mode. From then until 08 July 2005, $\sim$138000 Nm^3 (1 $Nm^3 \triangleq 10^6$ cm^3STP) of O_2-enriched aeration gas and $\sim$26000 Nm^3 of pressurized air were injected into the lake. A combination of O_2-enriched aeration gas and pressurized air was used for the first three weeks of the oxygenation mode to ensure a smooth transition from the preceding circulation support mode. Assuming that the composition of the aeration gas measured in July (Table 4) is representative of the entire oxygenation period in 2005, the total gas flux into Lake Hallwil from 05 April 2005 to 08 July 2005 corresponds to $\sim$160 t O_2. The masses M_i^{input} of He, Ne and Ar injected into the lake via the aeration gas input are listed in Table 6 alongside the estimated masses M_i^{excess} of excess noble gases dissolved in the water body. This comparison suggests that the mass of He injected into Lake Hallwil by the aeration system from 05 April 2005 to 08 July 2005 is in good agreement with the observed excess of He dissolved in the lake. Direct loss of injected aeration gas bubbles to the atmosphere seems therefore to be negligible. Again, it should be noted that visual observation of the lake during the oxygenation period confirmed the rather complete dissolution of the injected gas bubbles. Further, comparison of the injected noble gas excess with the local saturation concentrations expected below the thermocline at a depth of 15 m indicates that a steady state between artificial-gas injection and

Table 6. Comparison of the Masses of He, Ne and Ar Injected Into Lake Hallwil by the Aeration System With the Total Masses of Excess Noble Gases in the Lake

Gas i	M_i^{input} [a]	M_i^{excess} [b]	$\Delta = M_i^{excess}/M_i^{input}$
He	435 g	440 g	~100%
Ne	7.5 kg	8.5 kg	~110%
Ar	10 t	15 t	~150%

[a] M_i^{input}, total mass flux of gas i into Lake Hallwil from 05 April 2005 to 08 July 2005.

[b] M_i^{excess}, total mass of the excess of gas i in Lake Hallwil on 08 July 2005.

outgassing from the water phase would only be reached after more than 1 year of summer mode operation. Hence, such a hypothetical steady state never occurs in Lake Hallwil, as the gas excess is removed by the seasonal vertical mixing in winter. Therefore, in principle, the hypolimnion is able to store the total amount of gases injected during summer. For Ne and Ar, the gas excesses dissolved in the lake are slightly (Ne) and considerably (Ar) larger than the amounts input by the aeration system. However, the approach used here (i.e., estimating the total dissolved noble gas excess from three concentration profiles) is subject to large uncertainties. For instance, the linear interpolation used to infer the noble gas excesses at positions between the profiles might bias the results. To explore this effect, the mass balance calculations were repeated using only the plume and background profiles in the interpolation and ignoring the data from the far field site. The total masses of excess He, Ne and Ar derived from these calculations differ by ~20% from the results obtained using all three profiles. We expect the uncertainties of the mass balance calculations to lie within the range of these deviations. Given these uncertainties, the total masses of excess He and Ne in the lake appear to be equal to the masses injected by the aeration system, whereas the excess mass of Ar in the lake is significantly higher than the injected mass of Ar (Table 6). For He and Ne, the injected gas mass seems therefore to be retained mostly, or even completely, in the lake during aeration at the normal gas flow rate. By contrast, the high excess of dissolved Ar in Lake Hallwil cannot be explained solely by the input of Ar from the aeration system during oxygenation and its retention in the water column. As Ar is more soluble than He and Ne, it might also have partially dissolved from the larger bubbles of pressurized air that were injected into the lake during circulation support in the preceding winter and might even have accumulated in the "mixed" water column. In the case of Ar, it therefore appears that gas exchange at the lake surface is not fast enough to completely remove a gas excess that might be produced during the circulation period. As a result, the concentrations of dissolved Ar could not be entirely reset to atmospheric equilibrium concentrations. The deep water of Lake Hallwil is therefore expected to show a slight supersaturation with respect to Ar even at the beginning of the oxygenation period. This residual Ar excess might account for the difference between the mass of Ar injected by the aeration system and the mass of Ar dissolved in the lake that was observed in summer (Table 6).

[26] In the period of "high flow", the excess concentrations of noble gases at the plume site increased substantially. However, this short phase of increased aeration gas flow rate did not affect the far field and background profiles, and therefore seems to have influenced only a small volume at the center of the lake. We applied the same mass balance approach to assess the accumulation of noble gases in the water column close to the bubble plume at diffuser 6. These mass balances were calculated for a vertical water column centered at the plume site with an elliptic base that has the same width-to-length ratio as Lake Hallwil (see Figure 1). The volume of water concerned was varied to match the mass of noble gases injected through diffuser 6 during the 2 day period of high gas flow rate with the increase in the mass of dissolved noble gases stored in this adjusted water volume. The noble gas mass flux was calculated from the observed aeration gas flow rate (see Table 1) and from the aeration gas composition (Table 4). A volume corresponding to a vertical water column with an elliptic base measuring 340×66 m^2 must be chosen to obtain dissolved Ar concentrations that match the Ar input observed in the hypolimnion during the "high flow" phase. However, the increase in the He and Ne excesses in the same volume amounts to only ~75% of the gas mass injected by the aeration system. Part of the He and Ne input seems therefore to have been lost to the atmosphere. As mentioned, small gas bubbles escaping at the lake surface were observed during the "high flow" phase. The difference in the water column accumulation of Ar compared to He and Ne is consistent with a partial loss of aeration gas to the atmosphere. Due to its higher solubility, Ar is preferentially dissolved in water, whereas He and Ne tend to remain in the escaping bubbles. The solubility of O_2 is similar to that of Ar, and therefore O_2 contained in the injected bubbles is also expected to dissolve virtually completely in the water column, even at high-aeration gas flow rates.

[27] The mass balance calculations for the "high flow" phase showed that the aeration gas mass injected through diffuser 6 results in an accumulation of noble gases that is constrained to a relatively small water column around the bubble plume (footprint of $\sim 340 \times 66$ m^2). As diffusor 3 was operated in the same manner as diffusor 6, it is expected that both diffusors affected similar water volumes. The water volumes that are influenced by gas injection from each of the two active diffusers (diffuser 3 and 6; Figure 1) therefore do not overlap.

[28] The horizontal extension of the noble gas enrichment is controlled by water exchange associated with currents in the hypolimion. Basin-wide internal seiching has been suggested to lead to a dispersion of the "aeration plume signature" in Lake Hallwil. *McGinnis et al.* [2004] measured a period of ~6 h and a mean horizontal velocity of ~1 cm/s for the seiche-induced currents in the hypolimnion. The horizontal water displacement due to the seiche-induced currents over one period is therefore ~220 m. Hence, the spatial scale of the water mass affected by the gas excess is similar to the dispersion scale given by internal seiching over the 2 day period of high-aeration gas flow rate.

4. Conclusions

[29] Dissolved noble gases in eutrophic Lake Hallwil can be used as tracers to evaluate the characteristic physical processes of secondary gas exchange that are induced in the water column by artificial aeration, and to enable the

oxygenation efficiency of the aeration system to be quantified.

[30] It should be noted that the limited number of samples and the considerable changes in aeration gas flow rates that occurred during the observation period only allow a rough quantification of bubble-induced gas exchange based on the noble gas concentrations presented and on their spatial and temporal distribution patterns within Lake Hallwil. Nevertheless, the strong, distinct noble gas signals that are observed in the water column demonstrate the potential of noble gases as tracers not only to quantify natural gas exchange but also to investigate aeration systems in lakes. Similar studies using noble gases will help to promote the understanding of processes such as the seeping of gas into lakes and oceans [e.g., *Schubert et al.*, 2006; *Holzner et al.*, 2008]. Noble gas concentration profiles can be used to set additional boundary conditions that allow plume models for the analysis of gas/water interaction to be better constrained [*Wüest et al.*, 1992; *McGinnis et al.*, 2004] in order to optimize the operation of aeration systems.

[31] For future applications of noble gases in investigating the operation of aeration systems, we propose a refined sampling strategy that covers the entire oxygenation period during summer stratification. The first noble gas profiles should be sampled immediately before the aeration system is switched from "circulation" mode to "aeration" mode in order to define the initial (noble) gas concentrations prior to O_2 injection into the hypolimnion. Sampling should be repeated during the summer months, or at least at the end of the oxygenation period, to analyze the spatial and temporal evolution of noble gas concentrations in the lake. With extensive noble gas sampling, the total increase in the concentrations of noble gases in the hypolimnion might be interpretable as a quantitative measure of the total aeration gas mass that was effectively transferred to the lake water by bubble gas exchange.

[32] Noble gases in the pore water of lake sediments have been shown to preserve information on the history of the physical conditions prevailing in the overlying water column [*Brennwald*, 2004; *Brennwald et al.*, 2004]. The noble gas concentrations in the pore waters of the sediments of Lake Hallwil are therefore expected to have recorded the effects of the aeration operation since its implementation about 20 years ago [*Trösch et al.*, 2011].

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